

PATENT ABSTRACTS OF JAPAN

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(71)Applicant : FUJI ELECTRIC CO LTD

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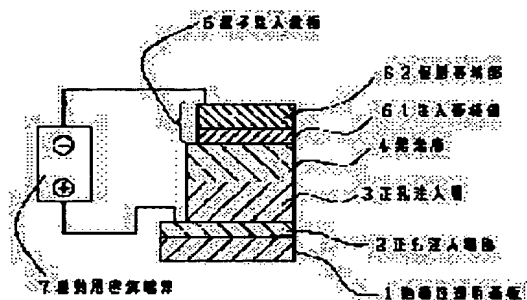
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(54) ORGANIC THIN FILM LUMINESCENT ELEMENT

(57)Abstract:

PURPOSE: To increase stability at the time of continuously emitting light by laminating a protection band and an implantation band, in one of an electron implanting electrode or positive hole implanting electrode.

CONSTITUTION: Glass or the like is used as an insulating transparent substrate 1, and a semitransparent film of Au and ITO or the like are formed by evaporation as a positive hole implanting electrode 2, to set a film thickness to 100 to 2000 \AA . In a positive hole implanting layer 3, a hydrazone compound is formed at about 300 to 800 \AA ; film thickness by resistance heating method or the like. By this constitution, adhesion of an implanting band is increased by a protective band, and an electron implanting electrode can be prevented from its separation, to increase stability of a device.



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CLAIMS

[Claim(s)]

[Claim 1] It is what it has the electrode of the couple of a hole-injection electrode and an electronic notes telegram pole, and the charge impregnation layer and luminous layer which were inserted into this electrode, and a charge impregnation layer receives impregnation of a charge from an electrode, and, subsequently to a luminous layer, carries out transport impregnation of this. It is the thing of the hole injection layer which receives impregnation of an electron hole from a hole-injection electrode, and the electronic injection layers which receive impregnation of an electron from an electronic notes telegram pole which contains a hole injection layer at least. It is the organic thin film light emitting device which a luminous layer emits light in predetermined wavelength in response to impregnation of an electron hole and an electron, and is characterized by an electronic notes telegram pole consisting of the impregnation band section and the guard-band section before long, as for the electrode of a couple.

[Claim 2] The organic thin film light emitting device characterized by the thickness of the impregnation band section being in 30 thru/or the range of 150A in an organic thin film light emitting device according to claim 1.

[Claim 3] The organic thin film light emitting device characterized by the impregnation band section consisting of a metal of 4eV or less of work functions in an organic thin film light emitting device according to claim 1.

[Claim 4] The organic thin film light emitting device characterized by the impregnation band section being a magnesium metal in an organic thin film light emitting device according to claim 3.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the organic thin film light emitting device used as a source of luminescence of various displays, especially relates to the electrode of an organic thin film light emitting device.

[0002]

[Description of the Prior Art] Development and utilization of various display devices are energetically advanced with rapid increase of the need of the flat display which changes to the conventional Braun tube. An electroluminescent element (it considers as an EL element below) is also based on such needs, and attention is attracted with the high resolution and the high visibility it is especially invisible on other displays as a spontaneous light emitting device of all solid-states.

[0003] Current and the thing put in practical use are EL elements which consist of an inorganic material which used the ZnS/Mn system for the luminous layer. However, since the driver voltage required for luminescence of this kind of inorganic EL element is as high as about 200V, the actuation approach becomes complicated and it has the trouble that a manufacturing cost is high. Moreover, since the effectiveness of blue luminescence is low, full-color-izing is difficult. On the other hand, since driver voltage required for luminescence can reduce substantially the thin film light emitting device using an organic material and it fully has the possibility of full-color-izing by addition of various luminescent material, research is activating it in recent years.

[0004] In the structure which carried out the laminating of a hole injection layer and the luminous layer, and vapor-deposited the alloy (mixing ratio 10:1) of Mg and Ag on this on the transparent electrode which consists of an indium-stannic-acid ghost (it omits Following ITO) especially By using tris (8-hydroxyquinoline) aluminum for luminescence material, and using a 1 and 1'-bis(4-N and N-JITORI aminophenyl) cyclohexane for hole-injection material They are 1000 cd/m² by the direct-current-voltage impression not more than 10V. Since the report that the above brightness was obtained was made, the spur has been applied to development. (Appl.Phys.Lett.51, 913, (1987)) Drawing 3 is the sectional view showing the conventional organic thin film light emitting device. the hole-injection electrode 2 which consists of transparence electric conduction film, such as an indium-stannic-acid ghost (Following ITO is called) and tin oxide, on the insulating transparence substrates 1, such as glass, — subsequently sequential membrane formation of a hole injection layer 3 and the luminous layer 4 is carried out. Finally the alloy of Mg, Ag, or Mg and In is formed as an electronic notes telegram pole 6.

[0005] Drawing 4 is the sectional view showing the organic thin film light emitting device concerning the example from which this invention differs. In order to raise electron injection nature and to raise luminous efficiency, the electronic injection layer 5 is formed. Generally the hole injection layer in these components, a luminous layer, and an electronic injection layer are formed by the resistance heating method. The same is said of an electronic notes telegram pole. This kind of component the plus side of the DC power supply for actuation by connecting a minus side to hole-injection electrodes, such as an ITO electrode, with electronic notes telegram poles, such as Mg/Ag. The electron hole poured in from this hole-injection electrode and the electron poured in from this electronic notes telegram pole are considered to emit light by radiation recombination in the luminous layer, and since the impregnation nature to the luminous layer of an electron hole improved especially by installation of a hole injection layer, that by which the extensive improvement of luminous efficiency was made is presumed.

[0006] Thus, although the organic thin film light emitting device has suggested strongly the possibility of low-battery actuation or full-color-izing, it needs to attain much more improvement in effectiveness, and multiple color-ization by amelioration of component structure, development of an organic material, etc. from now on. There is improvement in stability as an important problem turned to utilization on the other hand, and the problem of property degradation accompanying the prolonged actuation which is about 10,000 hours is the hurdle which must be overcome. Moreover, since an organic thin film is 1 micrometer or less, its membrane formation nature is good and it also needs development of an ingredient without the electric defect of a pinhole etc. Development of an organic material that it can furthermore mass-produce from a viewpoint of mass production nature and cheap and amelioration of the component formation approach are also important technical technical problems.

[0007] Examination of a work function is made in order to raise the electron injection nature from an electronic notes telegram pole to an organic layer for an improvement of luminous efficiency. For example, the alloy with which a work function contains a metal 4eV or less is indicated by JP,63-264692.A, JP,63-295695.A, and JP,2-15595.A. Especially, the alloy of Mg and Ag and the alloy of Mg and In are in use, and it was formed in 1000 thru/or the thickness of 3000A.

[0008]

[Problem(s) to be Solved by the Invention] However, when the above alloys of Mg and Ag and the alloy of Mg and In were used for an electronic notes telegram pole, there was a phenomenon in which an electronic notes telegram pole exfoliated in the continuation luminescence trial by long duration actuation of a component, and there was a problem that the dependability of a component was low. It is in offering the organic thin film light emitting device which this invention is made in view of an above-mentioned point, and that object prevents exfoliation of an electrode, and is excellent in long-term stability.

[0009]

[Means for Solving the Problem] It is what the above-mentioned object has the electrode of the couple of a hole-injection electrode and an electronic notes telegram pole, and the charge impregnation layer and luminous layer which were inserted into this electrode according to this invention, and a charge impregnation layer receives impregnation of a charge from an electrode, and, subsequently to a luminous layer, carries out transport impregnation of this. It is the thing of the hole injection layer which receives impregnation of an electron hole from a hole-injection electrode, and the electronic injection layers which receive impregnation of an electron from an electronic notes telegram pole which contains a hole injection layer at least. A luminous layer emits light in predetermined wavelength in response to impregnation of an electron hole and an electron, and the electrode of a couple is attained by supposing that an electronic notes telegram pole consists of the impregnation band section and the guard-band section before long.

[0010]

[Function] The guard-band section raises the adhesion of the impregnation band section, and prevents exfoliation of an electronic notes telegram pole.

[0011]

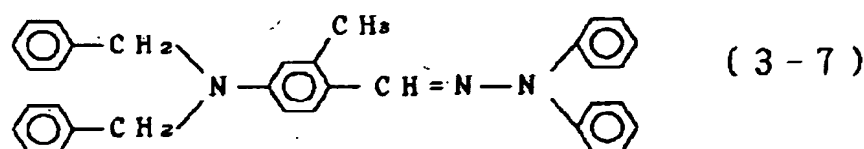
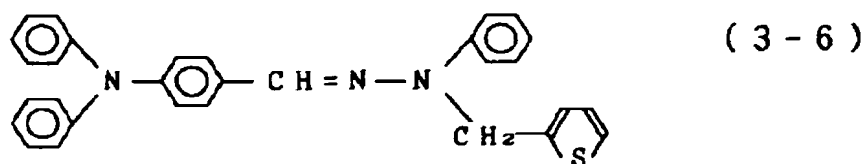
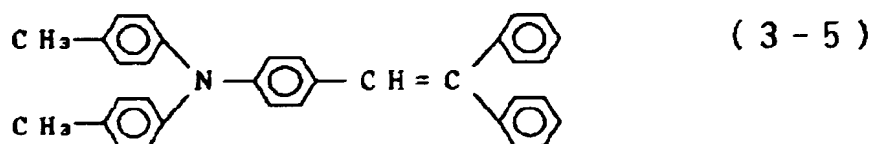
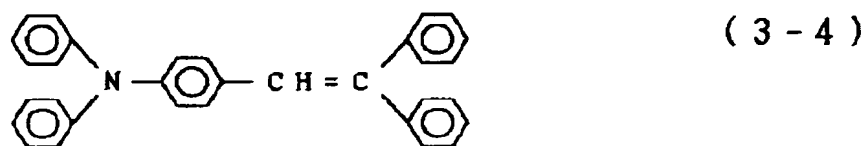
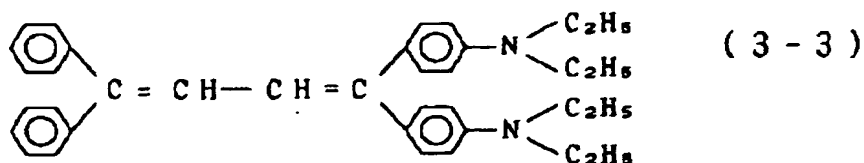
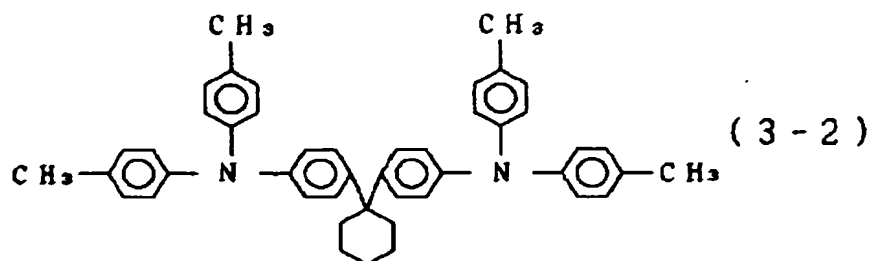
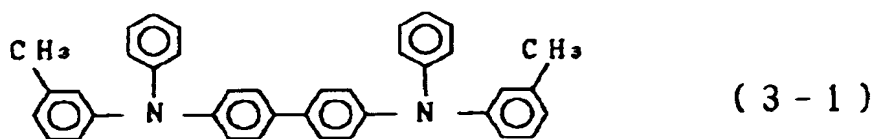
[Example] Next, the example of this invention is explained based on a drawing. Drawing 1 is the sectional view showing the organic thin film light emitting device concerning the example of this invention. Drawing 2 is the sectional view showing the organic thin film light emitting device concerning the example from which this invention differs. 1 — an insulating transparence substrate and 2 — for a luminous layer and 5, as for an electronic notes telegram pole and 61, an electronic injection layer and 6 are [a hole-injection electrode and 3 / a hole injection layer and 4 / the impregnation band section and 62] the guard-band sections.

[0012] The insulating transparence substrate 1 is the base material of an organic thin film light emitting device, and glass, resin, etc. are used. The hole-injection electrode 2 consists of transparence electric conduction film, such as semipermeable membrane, such as gold and nickel, and an indium-stannic-acid ghost (ITO), tin oxide (SnO₂), and is formed of resistance heating vacuum evaporatono, electron beam evaporation, a spatter, etc. 100 thru/or the thickness of thickness of 2000A are desirable.

[0013] In the maximal value of the light which conveyed the electron hole, poured into the luminous layer efficiently, and emitted light to it, the thing transparent as much as possible of a hole injection layer 3 is desirable. as the membrane formation approach — a spin coat, casting, and LB — although there are law, resistance heating vacuum evaporatono, electron beam evaporation, etc., resistance heating vacuum evaporatono is common. Thickness is 200 thru/or 5000A and is 300 thru/or 800A suitably. As hole-injection matter, a hydrazone compound, a pyrazoline compound, a stilbene compound, an amine system compound, etc. are used. The typical hole-injection matter is shown in a chemical formula (3-1) thru/or a chemical formula (3-7) below.

[0014]

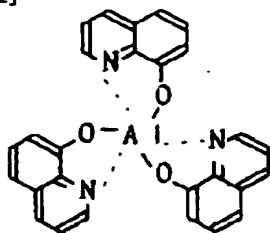
[Formula 1]



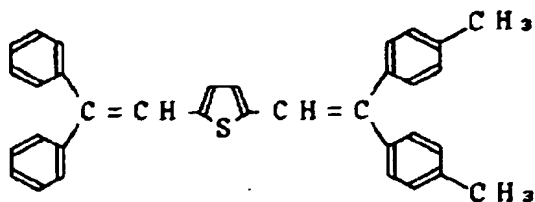
[0015] A luminous layer emits light efficiently with the electron poured in from the electron hole, electronic notes telegram pole, or electronic injection layer poured in from the hole injection layer. as the membrane formation approach — a spin coat, casting, and LB — although there are law, resistance heating vacuum evaporationo, electron beam evaporation, etc., resistance heating vacuum evaporationo is common. Thickness is 200 thru/or 5000A and is 300 thru/or 800A suitably.

[0016] As photogene, metal chelate compound, such as said tris (8-hydroxyquinoline) aluminum, a peri non derivative, a JISUCHIRIRU benzene derivative, etc. are used. Typical photogene is shown in a chemical formula (4-1) thru/or a chemical formula (4-5) below.

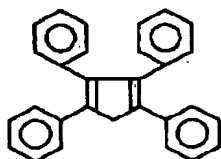
[0017]
[Formula 2]



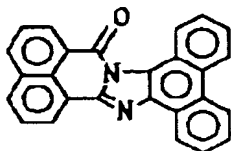
(4 - 1)



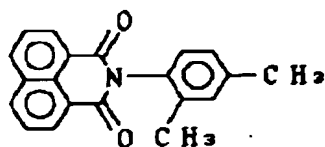
(4 - 2)



(4 - 3)



(4 - 4)



(4 - 5)

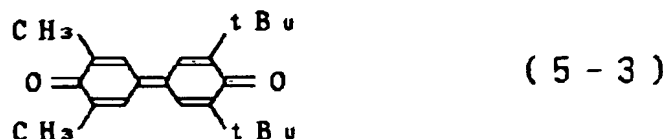
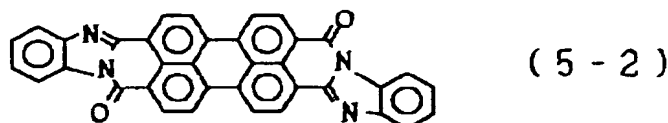
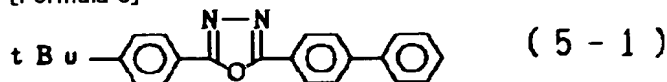
[0018] An electronic injection layer needs to convey and pour an electron into a luminous layer efficiently, as the membrane formation approach — a spin coat, casting, and LB — although there are low, resistance heating vacuum evaporation, electron beam evaporation, etc., resistance heating vacuum evaporation is common. Thickness is 200 thru/or 5000Å and is 300 thru/or 800Å suitably. As quality of an electronic notes receptacle, an OKISA diazole derivative, a perylene tetracarboxylic acid derivative, a diphenylquinone series compound, etc. are used. The typical quality of an electronic notes receptacle is shown in a chemical formula (5-1) thru/or a chemical formula (5-3).

[0019] A metal 4eV or less is used for the work function which is excellent in the electron injection nature to the luminous layer or charge impregnation layer of a substrate as the impregnation band section 61 of the electronic notes telegram pole 6 was mentioned above. Mg, In, calcium, Ti, Zr, etc. were the optimal as a result of the detailed experiment. Moreover, about the thickness of the impregnation band section, the remarkable stabilizing effect was obtained within the limits of 30 thru/or 150Å. That is, the exfoliation under continuation luminescence trial was brought forward in bigger thickness than 150Å, and the impregnation band section was formed in island shape in

thickness smaller than 30Å, and aggravation of the electron injection nature to a substrate layer was caused.
 [0020] About the guard-band section of the electronic notes telegram pole 6, with Ag, Au, Cu, aluminum, etc., the good result was obtained and remarkable effectiveness was acquired in 1000Å or more of thickness.

[0021]

[Formula 3]



[0022] The glass of 50mm angle which prepared the indium-stannic-acid ghost (ITO) of 2000Å of example 1 thickness was used as the substrate, this substrate was laid in resistance heating vacuum evaporation equipment, and membranes were formed in order of the hole injection layer 3 and the luminous layer 4. On the occasion of membrane formation, the inside of a vacuum tub was decompressed up to 8×10^{-4} Pa. To the hole injection layer, it heated the boat temperature 150 thru/or in 180 degrees C using the hole-injection matter shown in a chemical formula (3-1), and the membrane formation rate was carried out in 2Å/s, and was formed 600Å. To the luminous layer (8-hydroxyquinoline), it heated the boat temperature 250 thru/or in 350 degrees C using aluminum, and the membrane formation rate was carried out in 2Å/s, and was formed 600Å. After this, ejection and the stainless steel mask for dot patterns with a diameter of 5mm were attached from resistance heating vacuum evaporation equipment, the substrate was newly laid in resistance heating vacuum evaporation equipment, 1000Å of 50Å of Au (s) was continuously formed as the guard-band section 62 in Mg as the impregnation band section 61, and it considered as the electronic notes telegram pole 6.

The organic thin film light emitting device was created like the example 1 except forming 1000Å of Ag as the guard-band section in an example 2 electronic notes telegram pole.

The organic thin film light emitting device was created like the example 1 except forming 1000Å of aluminum as the guard-band section in an example 3 electronic notes telegram pole.

The organic thin film light emitting device was created like the example 1 except forming 1000Å of example of comparison 1 electronic notes telegram poles using Mg and In (mixing ratio rate 10 to 1).

After forming 2000Å of ITO(s) as a hole-injection electrode 2 on the glass substrate 1 of 450mm angle of examples, this ITO substrate was laid in vacuum devices like the example 1, and sequential creation was carried out with the hole injection layer 3, the luminous layer 4, and the electronic injection layer 5. 1000Å of guard-band sections which consist of Ag continuously the impregnation band section 61 which becomes the last from Mg as an electronic notes telegram pole 50Å was formed. The organic thin film light emitting device was formed like the example 1 using the matter shown with a chemical formula (5-1) as quality of an electronic notes receptacle except forming 400Å whenever [boat stoving temperature] by 3Å/s in 300 degrees C and membrane formation rate.

The organic thin film light emitting device was created like the example 4 except forming 1000Å of example of comparison 2 electronic notes telegram poles using Mg and In (mixing ratio rate 10 to 1). Thus, direct current voltage is impressed to the obtained organic thin film light emitting device, and it is 100 cd/m². Initial luminous efficiency and initial brightness 100 cd/m² which can be set The luminescence time amount when performing a continuation luminescence trial is shown in a table 1. All luminescence was green (main wavelength: 550nm) homogeneity luminescence.

[0023]

[A table 1]

	発光効率 (lm/W)	連続発光時間 (h)
実施例 1	1. 4 7	1 2 0 0
実施例 2	1. 4 3	1 1 0 0
実施例 3	1. 4 6	1 0 0 0
比較例 1	1. 5 2	1 5 0
実施例 4	1. 6 7	1 1 5 0
比較例 2	1. 7 3	2 0 0

It turns out that the organic thin film light emitting device which formed the electronic notes telegram pole from the guard-band section and the impregnation band section as seen in a table 1 shows remarkable stability in a continuation luminescence trial.

[0024]

[Effect of the Invention] It is what it has the electrode of the couple of a hole-injection electrode and an electronic notes telegram pole, and the charge impregnation layer and luminous layer which were inserted into this electrode according to this invention, and a charge impregnation layer receives impregnation of a charge from an electrode, and, subsequently to a luminous layer, carries out transport impregnation of this. It is the thing of the hole injection layer which receives impregnation of an electron hole from a hole-injection electrode, and the electronic injection layers which receive impregnation of an electron from an electronic notes telegram pole which contains a hole injection layer at least. A luminous layer emits light in predetermined wavelength in response to impregnation of an electron hole and an electron, and before long, since the electrode of a couple consists of the impregnation band section and the guard-band section, an electronic notes telegram pole Adhesion with the impregnation band section and a substrate layer is achieved by the guard-band section, and the organic thin film light emitting device which the exfoliation of an electronic notes telegram pole of is lost as a result, and is excellent in the stability at the time of continuation luminescence is obtained.

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] The sectional view showing the organic thin film light emitting device concerning the example of this invention

[Drawing 2] The sectional view showing the organic thin film light emitting device concerning the example from which this invention differs

[Drawing 3] The sectional view showing the conventional organic thin film light emitting device

[Drawing 4] The sectional view showing the organic thin film light emitting device from which the former differs

[Description of Notations]

1 Insulating Transparence Substrate

2 Hole-Injection Electrode

3 Hole Injection Layer

4 Luminous Layer

5 Electronic Injection Layer

6 Electronic Notes Telegram Pole

61 Impregnation Band Section

62 Guard-Band Section

[Translation done.]

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(71)出願人 00005234

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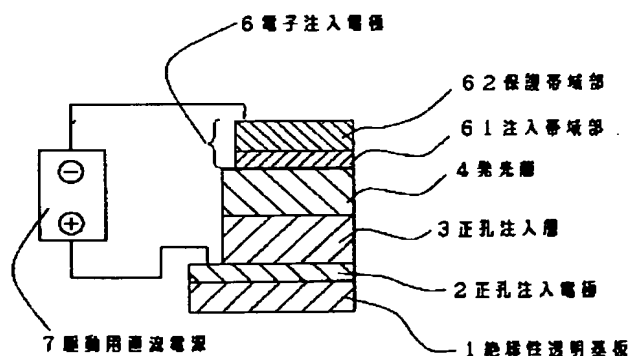
(74)代理人 弁理士 山口 巖

(54)【発明の名称】 有機薄膜発光素子

(57)【要約】

【目的】有機薄膜発光素子の連続発光時における安定性を高める。

【構成】電子注入電極6と正孔注入電極2の少なくとも一方の電極を保護帯域部と注入帯域部を積層して形成する。



【特許請求の範囲】

【請求項1】正孔注入電極および電子注入電極の一对の電極と、この電極に挟まれた電荷注入層と発光層とを有し、

電荷注入層は電極から電荷の注入を受け、次いでこれを発光層に輸送注入するもので、正孔注入電極から正孔の注入を受ける正孔注入層と電子注入電極から電子の注入を受ける電子注入層のうちの少なくとも正孔注入層を含むものであり、

発光層は正孔と電子の注入を受けて所定の波長の発光を行うものであり、

一对の電極はそのうち電子注入電極が注入帯域部と保護帯域部とからなることを特徴とする有機薄膜発光素子。

【請求項2】請求項1記載の有機薄膜発光素子において、注入帯域部の膜厚が30ないし150Åの範囲にあることを特徴とする有機薄膜発光素子。

【請求項3】請求項1記載の有機薄膜発光素子において、注入帯域部が仕事関数4eV以下の金属からなることを特徴とする有機薄膜発光素子。

【請求項4】請求項3記載の有機薄膜発光素子において、注入帯域部がマグネシウム金属であることを特徴とする有機薄膜発光素子。

【発明の詳細な説明】

【0001】

【産業上の利用分野】この発明は各種表示装置の発光源として用いられる有機薄膜発光素子に係り、特に有機薄膜発光素子の電極に関する。

【0002】

【従来の技術】従来のブラウン管にかわるフラットディスプレイの需要の急増に伴い、各種表示素子の開発及び実用化が精力的に進められている。エレクトロルミネッセンス素子（以下EL素子とする）もこうしたニーズに即するものであり、特に全固体の自発発光素子として、他のディスプレイにはない高解像度及び高視認性により注目を集めている。

【0003】現在、実用化されているものは、発光層にZnS/Mn系を用いた無機材料からなるEL素子である。しかるに、この種の無機EL素子は発光に必要な駆動電圧が200V程度と高いため駆動方法が複雑となり製造コストが高いといった問題点がある。また、青色発光の効率が低いため、フルカラー化が困難である。これに対して、有機材料を用いた薄膜発光素子は、発光に必要な駆動電圧が大幅に低減でき、かつ各種発光材料の添加によりフルカラー化の可能性を十分に持つことから、近年研究が活発化している。

【0004】特に、インジウムスズ酸化物（以下ITOと略する）からなる透明電極上に、正孔注入層と発光層を積層し、この上にMgとAgの合金（混合比10:1）を蒸着した構造において、発光材にトリス（8-ヒドロキシキノリン）アルミニウムを、正孔注入材に1、

1'-ビス（4-N, N-ジトリアミノフェニル）シクロヘキサンを用いることにより、10V以下の直流電圧印加で1000cd/m²以上の輝度が得られたという報告がなされて以来開発に拍車がかけられた。（Appl. Phys. Lett. 51, 913, (1987)）図3は従来の有機薄膜発光素子を示す断面図である。ガラス等の絶縁性透明基板1上にインジウムスズ酸化物（以下ITOと称する）、酸化スズ等の透明導電膜からなる正孔注入電極2、次いで正孔注入層3、発光層4を順次成膜する。最後に電子注入電極6としてMgとAgまたはMgとInの合金を形成する。

【0005】図4はこの発明の異なる実施例に係る有機薄膜発光素子を示す断面図である。電子注入性を向上させて発光効率を高めるために電子注入層5が設けられている。これらの素子における正孔注入層、発光層、電子注入層は一般的に抵抗加熱法により形成される。電子注入電極についても同様である。この種の素子は、駆動用直流電源のプラス側をITO電極等の正孔注入電極に、マイナス側をMg/Ag等の電子注入電極と接続することにより、該正孔注入電極から注入された正孔と該電子注入電極から注入された電子が発光層中で輻射再結合により発光するものと考えられており、特に正孔注入層の導入により、正孔の発光層への注入性が向上したため発光効率の大幅な改善がなされたものと推定されている。

【0006】このように有機薄膜発光素子は低電圧駆動やフルカラー化の可能性を強く示唆しているが今後素子構造の改良や有機材料の開発等により一層の効率向上と多色化を図る必要がある。一方実用化に向けての重要課題として安定性の向上があり1万時間程度の長時間駆動に伴う特性劣化の問題は乗り越えなければならないハードルである。また有機薄膜は1μm以下であるため成膜性が良好でピンホール等の電氣的欠陥のない材料の開発も必要である。さらに量産性の観点から大量生産が可能で安価な有機材料の開発や素子形成方法の改良も重要な技術課題である。

【0007】発光効率の改善のために電子注入電極から有機層への電子注入性を向上させるべく仕事関数の検討がなされている。例えば特開昭63-264692号公報、特開昭63-295695号公報、特開平2-15595号公報には仕事関数が4eV以下の金属を含む合金が開示されている。特にMgとAgの合金、MgとInの合金が主流であり、1000ないし3000Åの厚さに形成されていた。

【0008】

【発明が解決しようとする課題】しかしながら上述のようなMgとAgの合金、MgとInの合金を電子注入電極に使用した場合、素子の長時間駆動による連続発光試験において電子注入電極が剥離するという現象があり素子の信頼性が低いという問題があった。この発明は上述の点に鑑みてなされその目的は電極の剥離を防止して長

期の安定性に優れる有機薄膜発光素子を提供することにある。

【0009】

【課題を解決するための手段】 上述の目的はこの発明によれば正孔注入電極および電子注入電極の一対の電極と、この電極に挟まれた電荷注入層と発光層とを有し、電荷注入層は電極から電荷の注入を受け、ついでこれを発光層に輸送注入するもので、正孔注入電極から正孔の注入を受ける正孔注入層と電子注入電極から電子の注入を受ける電子注入層のうちの少なくとも正孔注入層を含むものであり、発光層は正孔と電子の注入を受けて所定の波長の発光を行うものであり、一対の電極はそのうち電子注入電極が注入帯域部と保護帯域部とからなるとすることにより達成される。

【0010】

【作用】 保護帯域部が注入帯域部の密着性を高めて電子注入電極の剥離を防止する。

【0011】

【実施例】 次にこの発明の実施例を図面に基づいて説明する。図1はこの発明の実施例に係る有機薄膜発光素子を示す断面図である。図2はこの発明の異なる実施例に係る有機薄膜発光素子を示す断面図である。1は絶縁性

透明基板、2は正孔注入電極、3は正孔注入層、4は発光層、5は電子注入層、6は電子注入電極、61は注入帯域部、62は保護帯域部である。

【0012】 絶縁性透明基板1は有機薄膜発光素子の支持体であり、ガラス、樹脂等が用いられる。正孔注入電極2は金、ニッケル等の半透膜やインジウムスズ酸化物(ITO)、酸化スズ(SnO₂)等の透明導電膜からなり、抵抗加熱蒸着、電子ビーム蒸着、スパッタ法等により形成される。膜厚は100ないし2000Åの厚さが好ましい。

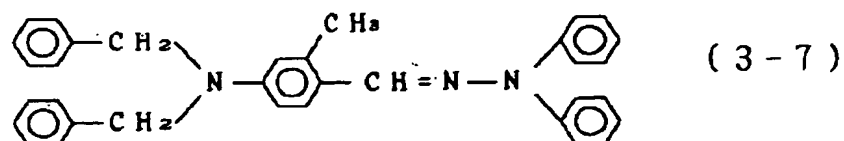
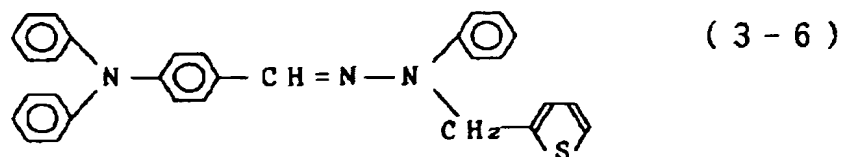
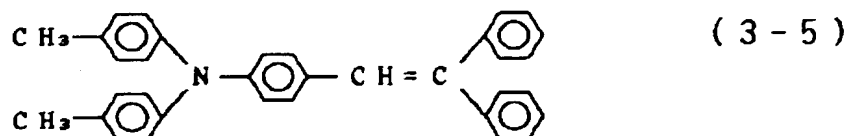
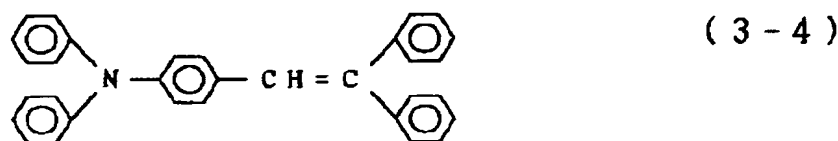
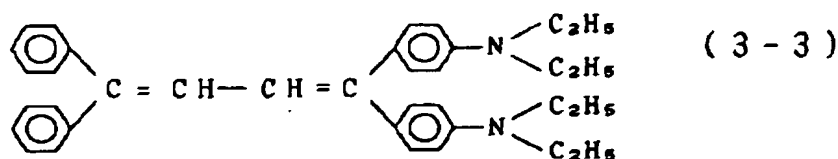
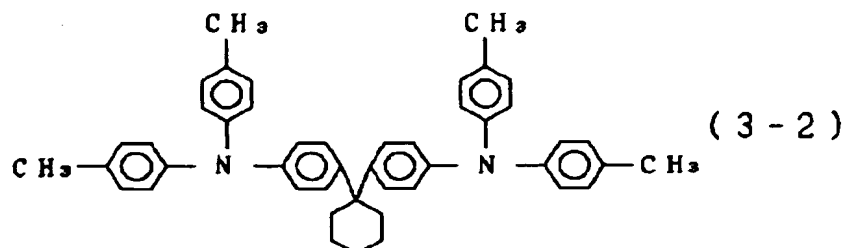
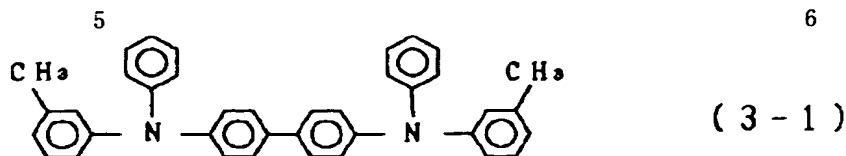
【0013】 正孔注入層3は発光層に効率良く正孔を輸送、注入し発光した光の極大値において出来るだけ透明であることが望ましい。成膜方法としてはスピコート、キャスト、LB法、抵抗加熱蒸着、電子ビーム蒸着等があるが抵抗加熱蒸着が一般的である。膜厚は200ないし5000Åであり、好適には300ないし800Åである。正孔注入物質としてはヒドラゾン化合物、ピラゾリン化合物、スチルベン化合物、アミン系化合物などが用いられる。代表的な正孔注入物質が以下化学式(3-1)ないし化学式(3-7)に示される。

【0014】

【化1】

(4)

6

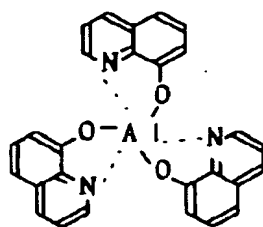


【0015】発光層は正孔注入層より注入された正孔と電子注入電極または電子注入層から注入された電子により効率良く発光を行う。成膜方法としてはスピコート、キャスト、LB法、抵抗加熱蒸着、電子ビーム蒸着等があるが抵抗加熱蒸着が一般的である。膜厚は200ないし5000Åであり、好適には300ないし800Åである。

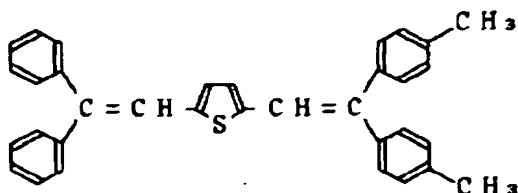
【0016】発光物質としては前記トリス(8-ヒドロキシキノリン)アルミニウム等の金属キレート化合物やペリノン誘導体、ジスチルベンゼン誘導体、等が用いられる。代表的な発光物質が以下化学式(4-1)ないし化学式(4-5)に示される。

【0017】

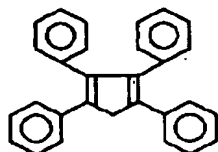
【化2】



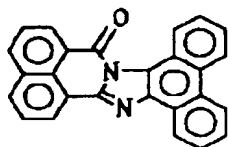
(4-1)



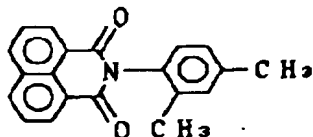
(4-2)



(4-3)



(4-4)



(4-5)

【0018】電子注入層は電子を発光層に効率良く輸送、注入することが必要である。成膜方法としてはスピンコート、キャスト、LB法、抵抗加熱蒸着、電子ビーム蒸着等があるが抵抗加熱蒸着が一般的である。膜厚は200ないし5000Åであり、好適には300ないし800Åである。電子注入物質としてはオキサジアゾール誘導体、ペリレンテトラカルボン酸誘導体、ジフェノキノン系化合物などが用いられる。代表的な電子注入物質が化学式(5-1)ないし化学式(5-3)に示される。

【0019】電子注入電極6の注入帯域部61は前述し

40 たように下地の発光層または電荷注入層への電子注入性に優れる仕事関数が4eV以下の金属が用いられる。詳細な実験の結果Mg, In, Ca, Ti, Zr等が最適であった。また注入帯域部の膜厚については30ないし150Åの範囲内において顕著な安定効果が得られた。即ち150Åよりも大きな膜厚においては連続発光試験中の剥離が早まり、また30Åよりも小さな膜厚においては注入帯域部が島状に形成され下地層への電子注入性の悪化を招いた。

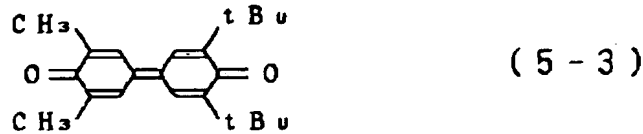
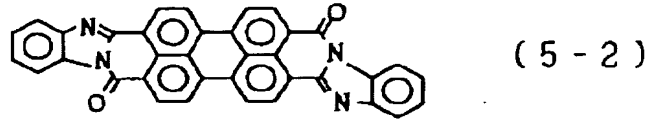
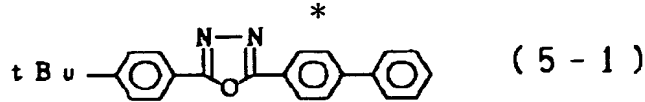
【0020】電子注入電極6の保護帯域部についてはAg, Au, Cu, Al等で良好な結果が得られ、膜厚1

50

000 Å 以上において顕著な効果が得られた。

【0021】

*【化3】



【0022】実施例1

膜厚2000 Åのインジウムスズ酸化物 (ITO) を設けた50mm角のガラスを基板とし、この基板を抵抗加熱蒸着装置内に載置し、正孔注入層3、発光層4の順に成膜した。成膜に際して真空槽内は 8×10^{-4} Paまで減圧した。正孔注入層には化学式(3-1)に示される正孔注入物質を用い、ポート温度150ないし180℃の範囲で加熱し、成膜速度を2 Å/sとして600 Å形成した。発光層には(8-ヒドロキシキノリン)アルミニウムを用い、ポート温度250ないし350℃の範囲で加熱し、成膜速度を2 Å/sとして600 Å形成した。このあと基板を抵抗加熱蒸着装置から取り出し、直径5mmのドットパターン用ステンレスマスクを取り付け、新たに抵抗加熱蒸着装置内に載置し、注入帯域部61としてMgを50 Å、続いて保護帯域部62としてAuを1000 Å形成し電子注入電極6とした。

実施例2

電子注入電極における保護帯域部としてAgを1000 Å形成する以外は実施例1と同様にして有機薄膜発光素子を作成した。

実施例3

電子注入電極における保護帯域部としてAlを1000 Å形成する以外は実施例1と同様にして有機薄膜発光素子を作成した。

比較例1

電子注入電極をMgとIn (混合比率10対1) を用いて1000 Å形成する以外は実施例1と同様にして有機薄膜発光素子を作成した。

実施例4

50mm角のガラス基板1上に正孔注入電極2としてITOを2000 Å形成したのち、このITO基板を実施例1と同様にして真空装置内に載置し、正孔注入層3、発光層4、電子注入層5と順次作成した。最後に電子注入電極としてMgからなる注入帯域部61を50 Å、続いてAgからなる保護帯域部を1000 Å形成した。電子注入物質として化学式(5-1)で示される物質を用い、ポート加熱温度300℃、成膜速度3 Å/sにて400 Å形成する以外は実施例1と同様にして有機薄膜発光素子を作成した。

比較例2

電子注入電極をMgとIn (混合比率10対1) を用いて1000 Å形成する以外は実施例4と同様にして有機薄膜発光素子を作成した。このようにして得られた有機薄膜発光素子に直流電圧を印加し、100 cd/m²における初期発光効率と初期輝度100 cd/m²にて連続発光試験を行ったときの発光時間を表1に示す。発光は全て緑色 (中心波長: 550 nm) の均一発光であった。

【0023】

【表1】

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	発光効率 (lm/W)	連続発光時間 (h)
実施例1	1.47	1200
実施例2	1.43	1100
実施例3	1.46	1000
比較例1	1.52	150
実施例4	1.67	1150
比較例2	1.73	200

表1に見られるように電子注入電極を保護帯域部と注入帯域部とから形成した有機薄膜発光素子は連続発光試験において顕著な安定性を示すことがわかる。

【0024】

【発明の効果】この発明によれば正孔注入電極および電子注入電極の一对の電極と、この電極に挟まれた電荷注入層と発光層とを有し、電荷注入層は電極から電荷の注入を受け、次いでこれを発光層に輸送注入するもので、正孔注入電極から正孔の注入を受ける正孔注入層と電子注入電極から電子の注入を受ける電子注入層のうちの少なくとも正孔注入層を含むものであり、発光層は正孔と電子の注入を受けて所定の波長の発光を行うものであり、一对の電極はそのうち電子注入電極が注入帯域部と保護帯域部とからなるので、保護帯域部により注入帯域部と下地層との密着が図られ、その結果電子注入電極の剥離がなくなって連続発光時の安定性に優れた有機薄膜発光素子が得られる。

*

*【図面の簡単な説明】

【図1】この発明の実施例に係る有機薄膜発光素子を示す断面図

【図2】この発明の異なる実施例に係る有機薄膜発光素子を示す断面図

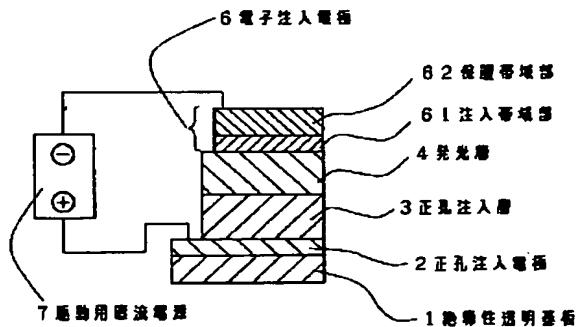
【図3】従来の有機薄膜発光素子を示す断面図

【図4】従来の異なる有機薄膜発光素子を示す断面図

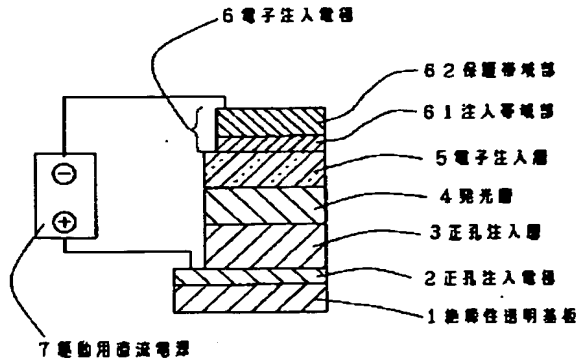
【符号の説明】

- 20 1 絶縁性透明基板
2 正孔注入電極
3 正孔注入層
4 発光層
5 電子注入層
6 電子注入電極
61 注入帯域部
62 保護帯域部

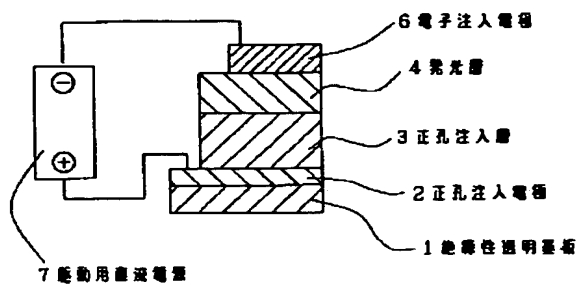
【図1】



【図2】



【図3】



【図4】

